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STUDY OF THE INTERACTION OF ELECTROMAGNETIC RADIATION WITH MATT--ETC (1)

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Introduction

During the tenure of Grants G174 and G181, three separate activities dominated, of which the largest was the study of transient molecules by double resonance spectroscopy. The other two were work on acoustic imaging by Bragg diffraction and a theoretical study of internal wave generation by wake collapse in a stratified fluid. In addition we sponsored (jointly with the Chemistry Department) visits by the distinguished theoretical chemist, Dr. J.O. Hirschfelder. Reports on these separate activities follow.

A. Double Resonance Spectroscopy

A laboratory for the study of transient molecules by tunable laser and microwave-laser double resonance spectroscopy was established within the Quantum Institute.

Initially the research involved joint efforts between the Departments of Physics and Chemistry. At present the laboratory is functioning under the direction of Professor David Harris, with three postdoctoral fellows and five graduate students. A summary of the finished projects which were worked on follows.

(a) CW Dye Laser Excitation Spectroscopy: CaF $A^2\Pi$ - $X^2\Sigma$

Excitation spectra of the CaF $A^2\Pi$ - $X^2\Sigma$ (0,0), (1,1), and (1,0) bands have been observed and assigned. A previous rotational analysis of the CaF A - X and B - X bands was shown to be incorrect. Because it is possible to make independent rotational assignments of each line in an excitation spectrum by observing frequency differences and relative intensities in photoluminescence spectra, tunable laser excitation spectroscopy promises much less ambiguity than traditional techniques for assignment of dense, badly overlapped spectra.

The following spectroscopic constants (in cm^{-1}) were obtained for the CaF $A^2\Pi$ and $X^2\Sigma$ states. Numbers in parentheses correspond to three standard deviations uncertainty in the last digit.

	$X^2\Sigma$	$A^2\Pi$
ν_{∞}		$^2\Pi_{1/2}$ 16493.1(6)
		$^2\Pi_{3/2}$ 16565.6(6)
$\Delta G_{1/2}$	581.1(9)	$^2\Pi_{1/2}$ 586.8(9)
Be	0.3385(11)	0.3436(12)
$B_e^{\text{eff}} (J=3/2) - B_e^{\text{eff}} (J=1/2)$	---	0.00312(21)
α_e	0.00255(48)	0.00283(45)
D (estimated)	4.44×10^{-7}	4.55×10^{-7}
γ (spin-rotation)	$ \gamma < 3 \times 10^{-3}$	---
A_O (spin-orbit)	---	73.4(9)
p (lambda doubling)	---	- 0.045(4)

The origin of the $A^2\Pi_{1/2} - X^2\Sigma$ (1,1) subband lies $5.54(30) \text{ cm}^{-1}$ to the blue of the corresponding (0,0) subband origin. The (0,0) band Q_2 head is observed to form at $J = 26 \pm 0.5$. The difference of the $A^2\Pi$ effective rotational constants is $2B^2/A$. The $A^2\Pi$ lambda doubling constant, p, agrees well with the pure precession estimate of the interaction between the $A^2\Pi$ and $B^2\Sigma$ states.

(b) Laser Induced Fluorescence and Optical-Optical Double Resonance of MgO.

An Ar^+ laser and tunable dye laser have been utilized for the study of various electronic states of MgO. It was discovered that the 4765 \AA line of Ar^+ laser excites three transitions of ^{24}MgO in the $B^1\Sigma^+ - X^1\Sigma^+$ system, namely R(26) of the (5-4) band, R(49) of the (4-3) band and R(69) of the (3-2) band. The 4965 \AA

line almost exclusively excited R(36) of the (2-2) band of ^{26}MgO (11% natural abundance) also in the B-X system. A large number of the fluorescence bands in the $B^1\Sigma^+$ - $A^1\Pi$ system, as well as in the B-X system have been detected and assigned. By use of a tunable dye laser we were able to excite individual lines in the B-A system and thus detect molecules populated in the electronically-excited $A^1\Pi$ states which are present in the flame produced by Mg + N_2O . Finally, optical-optical double resonance, which was recently observed for BaO in this laboratory, was successfully demonstrated for ^{26}MgO . The dye laser beam is directed to the flame colinearly with the Ar^+ laser beam of 4965 Å, and its frequency scanned. The double resonance is detectable as a sudden increase in ultraviolet emission (P and R bands) at two different frequencies of the dye laser corresponding to the R and P branches of a particular rotational transition. They correspond to R(37) and P(37) between the (B, $v'' = 2$) and (E, $v' = 1$) states. The uv photoluminescence has been analyzed through a monochromator and the band progressions in the E-X and the E-A system have been observed. The symmetry of the upper state is confirmed as $E^1\Sigma^+$. The dye laser P-R separation gives the rotational constant of the upper state of ^{26}MgO , and it is in good agreement (after correction for isotope effects) with the result recently reported for the (E, $v = 0$) state of ^{24}MgO . The harmonic frequency ω_e of the E-state of ^{26}MgO is estimated as $712 \pm 10 \text{ cm}^{-1}$.

Many of the lines of the B-X system observed by photoluminescence show systematic deviations caused by perturbations. The perturbations are due to the $^3\Pi$ state interacting with the $X^1\Sigma$ ground state. For the strongly perturbed levels we have observed transitions to the perturbing levels as well by intensity borrowing by the mixing of the wave functions associated with the two states. An analysis of the perturbations has yielded the following spectroscopic constants for $MgO(a^3\Pi)$: (in cm^{-1}).

$$T_e = 2611$$

$$\omega_e = 656$$

$$\omega_{eX_e} = 5.2$$

$$B_e = 0.504$$

$$A = -63.7$$

(c) Optical-Optical Double Resonance Spectroscopy of BaO.

When BaO is irradiated simultaneously with the 488 or 496.5 nm line of an Ar^+ laser and the output of a wavelength-scanned (565 - 620 nm) continuous wave dye laser, an optical-optical double resonance (OODR) excitation spectrum is obtained. Photoluminescence progressions, excited by the resonant, sequential absorption of two visible photons, are observed extending from 250 - 900 nm. OODR extends tunable laser excitation spectroscopy to electronic states more than 5 eV above the electronic ground state. The highest vibrational level previously observed in the barium oxide ground state was $X^1\Sigma$ ($v'' = 17$). Vibrational energies and rotational constants obtained from OODR photoluminescence spectra were used to construct an RKR potential energy curve for

BaO $X^1\Sigma$ which will accurately locate the intersection between the $X^1\Sigma^+$ and the $a^3\Pi_i$ curves.

OODR excitation spectroscopy revealed 17 previously unobserved vibronic levels of $^1\Sigma^+$ electronic symmetry between 36500 and 38600 cm^{-1} above BaO $X^1\Sigma$ ($v'' = 0, J'' = 0$). These levels belong to two or more perturbed electronic states; one of which may be the upper state in the BaO Parkinson bands, previously identified as $B(^1\Pi)$.

The spectra obtained from OODR are relatively simple, consisting at most of three transitions [$R(J')$, $Q(J')$, $P(J')$] for each two photon-excited vibronic level:

$$(v', J') \rightarrow (v^*, J^* = J' \pm 1, 0).$$

The rotational constant of the final excited level is obtained from

$$B^* = [R(J') - P(J')] / (4J' + 2),$$

if the (v^*, J^*) level is free of perturbations. Optical-optical double resonance is a powerful and promising tool for the study of excited electronic states.

(d) Microwave Optical Double Resonance (MODR) of BaO.

In the microwave optical double resonance experiments carried out in our laboratory, ground state molecules are pumped by visible light from a cw laser to a specific rotational and vibrational level of an excited electronic state. Visible emission arising from the molecules in the pumped state - photoluminescence - is monitored by a photomultiplier tube; a microwave transition from a rotational level adjacent to either the ground state depopulated level or the excited state pumped level is detected by a change in the wavelength, intensity or polarization of the detected photoluminescence. Under these conditions, the absorption of a microwave photon with an energy of about $1/200$ of kT (at 300°K) is observed by the detection of an optical photon of energy which is approximately 100 times kT . The MODR system acts as amplifier. Further the Doppler width of the microwave transition is insignificant relative to the width arising from lifetime, saturation, pressure, or wall broadening mechanisms. Effectively, MODR combines the high sensitivity of optical spectroscopy with the high resolution of microwave spectroscopy. Also, since MODR spectroscopy is a double resonance phenomenon which involves three levels rather than the usual two, it is useful for assigning rotational levels of complex spectra. Suppose for example, that the microwave frequency is tuned to a known ground state rotational transition. If the laser frequency is then tuned until a MODR signal is observed, the selection rules limit the assignment of the upper state of the optical transition to only a few possible choices. If the laser frequency is then held fixed and the

microwave frequency tuned until an excited state MODR signal is observed, the selection rules again limit the assignment of the quantum numbers of the excited state transition to only a few possible choices. By repeating this process, the excited state spectrum can be characterized.

Rotational transition frequencies and the resultant rotational constants for the BaO $X^1\Sigma$ and $A^1\Sigma$ states are listed below.

Observed MODR transitions in BaO $X^1\Sigma$ and $A^1\Sigma$

Electronic state	v	Transition $J \rightarrow J + 1$	Measured frequency (MHz)	B_v (MHz)
$X^1\Sigma$	0	0 - 1	18702. (1)	
		1 - 2	37404. (1)	
		2 - 3	56106. (1)	9351.1
	1	2 - 3	55855. (2)	9309.3
$A^1\Sigma$	0	2 - 3	46376. (2)	7729.5
		1 - 2	30760.5 (1)	
		2 - 3	46142. (1)	7690.3
	$^{137}\text{Ba}^{16}\text{O}$	2 - 3	46177.7 (1)	7696.4
		2 - 3	45986. (1)	7664.5
	2	1 - 2	30493. (2)	
		2 - 3	45740. (1)	
		3 - 4	60984.5 (1.5)	
		4 - 5	76226.8 (1.5)	7623.3
		2 - 3	45551. (1)	7592.0
	4	2 - 3	45397.3 (1)	7566.4
		1 - 2	29927.6 ^b	
	7	2 - 3	44891.4 ^b	7482.0

Uncertainties in () are two standard deviations.

(e) MODR and Laser Excitation Spectroscopy of NO₂

A rotational assignment of approximately 80 lines with $K_a' = 0, 1, 2, 3$, and 4 has been made of the 593 nm $^2A_1 \rightarrow ^2B_2$ band of NO₂ using cw dye laser excitation and microwave optical double-resonance spectroscopy. Rotational constants for the 2B_2 state

were obtained as $A = 8.52 \text{ cm}^{-1}$, $B = 0.458 \text{ cm}^{-1}$, and $C = 0.388 \text{ cm}^{-1}$. Spin splittings for the $K_A' = 0$ excited state levels fit a simple symmetric top formula and give $(\Delta B_1 + \Delta C) = -0.648 \text{ cm}^{-1}$. Spin splittings for $K_A' = 1$ (N' even) are irregular and are shown to change sign between $N' = 6$ and 8. Assuming that the large inertial defect of 4.66 amu \AA^2 arises solely from A , a structure for the $'B_1$ state is obtained which gives $r(\text{N-O}) = 1.35 \text{ \AA}$ and an O-N-O angle of 105° . Alternatively, weighting the three rotational constants equally gives $r = 1.29 \text{ \AA}$ and $\theta = 118^\circ$.

An interesting pressure dependence of the MODR signal for the $'B_1$ $9_{0,0}-8_{1,0}$ transition was found and analyzed in terms of a three-level state kinetic treatment of microwave optical double resonance. The analysis shows that the $8_{1,0}$ level has considerably lower photon yield for photoluminescence than the $9_{0,0}$ level. In addition to the $9_{0,0}-8_{1,0}$ transitions, three groups of mystery transitions originating from the $9_{0,0}$ or $8_{1,0}$ level were unexpectedly detected. The final levels of these transitions cannot belong to the same vibronic state as the $9_{0,0}$ and $8_{1,0}$ states. A reasonable explanation is that the mystery transitions are perturbation induced microwave transitions from levels of the $'B_1$ state to levels of a longer lived electronic state. Different photon yields of the $9_{0,0}$ and $8_{1,0}$ rotational levels of the $'B_1$ state are also understood by perturbations between the $'B_1$ and the longer lived electronic state.

B. Ultrasonic Imaging

The goal of this research was to work towards a practical ultrasonic system for the visualization of the internal structure of human organs and tissue for medical diagnostic purposes. The work progressed to the point that we were able to develop a real-time orthographic acoustic imaging system. As the mechanism for conversion of an acoustic pattern into a light pattern, the system employed Bragg-diffraction of laser light by the acoustic waves which had been scattered from the objects to be imaged.

The work prior to 1972 had involved research on a system operating at an ultrasonic frequency of 15MHz and above. The work subsequent to 1972 was to reduce the ultrasonic frequency of operation to 5MHz or below specifically for the purpose of developing a capability in medical diagnosis. This latter system was developed to the point of producing both reflection and transmission images in either a pulsed or continuous-wave mode of operation.

In addition to the above experimental work, we also performed theoretical analyses involving noise limitations and sensitivity. We were interested particularly in probing inherent weaknesses in the Bragg-diffraction imaging systems and in making comparisons between this type of system and competing types. As a result of the theoretical work, we eventually discovered that Bragg-diffraction systems suffer from a kind of insensitivity inherent in all systems in which the readout involves interaction with laser light. Our analyses show that this statement applies as well to the dynamic-ripple diffraction systems of Zenith and the static-ripple diffraction systems of Holosonics. Due to the high quantum noise associated

with laser-beam photons, these systems are inherently more noisy than those employing fundamental scanning modes in which the read-out is accomplished by piezoelectric transducers, where the chief noise is thermal.

As part of the work on this project we also developed a capability for digital processing of images. Using a variety of techniques in this regard, such as histogram equalization and contrast enhancement, we have eventually been able to improve the quality of our acoustic images. However, this work is still in a rather early research stage and needs to be further developed before digital processing of Bragg-diffraction images can be employed in a practical way.

C. Wake Collapse

The problem of internal wave generation by the collapse of a mixed wake region in a density-stratified fluid is of both theoretical and practical interest. Elaborate computer programs exist, but they give little insight into the collapsed structure, and have limited applicability. We undertook to approach the problem from the other end, asking whether there is any useful regime in which the hydrodynamic problem is exactly soluble. It turned out that the linearized problem (weak density gradient) with an infinite cylindrical wake having sharp boundaries, is in fact exactly soluble, and that the solution has unexpected features, in particular near the wake boundary. There has been some recent experimental confirmation of these results.

D. Visits by Hirschfelder

The Quantum Institute, in conjunction with the Chemistry Department, sponsored visits by Professor J. O. Hirschfelder in each winter quarter, as a distinguished visiting scientist.

Dr. Hirschfelder, regularly a faculty member at the University of Wisconsin, is a member of the National Academy of Sciences who has done significant work in a wide range of fields. His breadth of interest translated itself into valuable interactions with faculty and students in Engineering, Chemistry and Physics. Dr. Hirschfelder thus served as a catalyst, inducing scientists of separate disciplines to think about common problems. This is precisely that role we hoped the visitors sponsored by the Quantum Institute would play. In addition, Dr. Hirschfelder took part in our ongoing quantum mechanics group meetings, and collaborated with Professor Palke in joint work on the use of QM Streamlines in Barrier Problems.

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